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CRACK ARRESTMENT COMPOUNDS OF CORROSION FATIGUE FOR HIGH STRENGTH 4340 STEEL

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

It has been shown that the fatigue life of a high strength Type 4340 steel exposed to high humidity is reduced by an order of magnitude when compared to dry ambient air. This has been directly attributed to the effects of corrosion and hydrogen embrittlement. In the present work, the principles of process control, which affect the electrochemical reactions occurring at the tip of the advancing crack, are integrated with the metallurgical concepts of the stress cracking phenomena to develop new crack arrestment

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compounds. The concept of phase transfer catalysis has been used to solubilize inorganic inhibitors into an organic phase. This enabled the inhibitor ions to remain free of hydration shells and become more effective inhibitors. It has been demonstrated that a number of combinations of compounds such as those containing chromate, borate and nitrite, or nitrite, borate and cerate have been successful in retarding the fatigue crack growth rate of Type 4340 steel exposed to 90% relative humidity.

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INTRODUCTION

BACKGROUND

The catastrophic damage caused by sudden failures of high strength steel naval aircraft parts due to environmental effects has long been recognized as a major material problem. Early emphasis focused on improving mechanical properties of the alloys to compensate for this effect of environment. However, it was soon realized that increasing the strength of the steels also increased their susceptibility to environmental cracking or fatigue failures. Subsequent studies concentrated on the interplay of corrosion processes occurring at crack tips or areas of high stress concentrations. Among the electrochemical reactions occurring at this interface, the most common and damaging is the hydrogen reduction process where hydrated protons are discharged to neutral hydrogen atoms. The cathodic reactions involved are:

$$H_3O^+ + e(M) \rightarrow MH_{ads} + H_2O \text{ (in acids)} \tag{1}$$

or

$$H_2O + e(M) \rightarrow MH_{ads} + OH^- \text{ (in neutral or alkaline media)} \tag{2}$$

$$MH_{ads} \rightarrow MH_{abs} \text{ (Diffusion Process)} \tag{3}$$

It is in Step (3) that the adsorbed atomic hydrogen (MH_{ads}) diffusing into the metal somehow reacts and causes embrittlement. This loss of toughness can cause the part to fail prematurely. Hydrogen is becoming recognized as the greatest single source of damage in high strength structural aircraft failures. As the demand for high performance reliability aircraft increases, the knowledge of hydrogen embrittlement effects and the methods to prevent it become more vital. It is also generally accepted that every crack that ultimately grows to catastrophic failure is environmentally induced because such cracks contain a condensed phase of moisture of usually low pH, produced either by the environment or by the corrosion processes at the tip.

A study has been made on the feasibility of formulating new compounds that can be applied *in situ* to arrest crack propagation. The properties of these compounds would be such that they act to: (1) inhibit moisture entry at the crack tip—thereby inhibiting corrosion, (2) modify the interfacial chemistry in such a way that the atomic hydrogen evolved from corrosion reactions is removed immediately—thereby impeding its entry into the metal, and (3) create a chemical barrier (passive film) at the crack surface.

To date, most of the work done in developing inhibitors of corrosion fatigue or stress corrosion cracking (SCC) use inorganic compounds dissolved in aqueous media.[1,2] In the ionic state, these compounds are surrounded by a shell of water molecules. This increases the size of the inhibiting ions thus restricting their migration to the reaction interface. Therefore, only a fraction of these ions can reach the metal surface and can perform their function as inhibitors. In the present study, this problem of hydration shell has been eliminated by dissolving the inorganic compounds in a nonaqueous medium.

In another program[3] at this laboratory, a method was developed by which metal anions could be solubilized in organic media using phase transfer catalysts. This method provides a means of evaluating some candidate corrosion inhibiting ions without introducing water into the crack propagating system. This approach also eliminates questions concerning hydration shells of inhibiting ions completely from the reaction interface. Thus, a study has been made, using an integrated mechanistic approach of both the electrochemical and metallurgical considerations to develop new inhibitors for crack arrestment in Type 4340 steel in the fatigue mode.

EXPERIMENTAL PROCEDURE

Potential crack arrestment and corrosion inhibiting compounds considered here were selected on the basis of the following considerations:

1. The compound is a passivator——makes an active surface passive through anodic oxidation and formation of a barrier passive film.

2. The compound is a buffer——buffers the pH of the condensed moisture at the crack tip to near neutral condition.

3. The compound is an effective hydrogen getter or hydride former[4]——forms hydride or other compound from the nascent hydrogen evolved during electrochemical reduction of proton (H^+) before it is able to enter into the metal.

4. The compound functions as a negative catalyst for hydrogen overvoltage[5]—— the presence of a foreign metal at the crack tip accelerates the hydrogen recombination reaction to form molecular hydrogen.

5. The compound increases surface-energy at the tip of the crack[6,7] produced from static or cyclic loading (from 'Rebinder Effect').

6. The compound is a water displacing organic vehicle such as mineral spirits, and acts as the solvent for the above specialized anions and cations.

The phase transfer catalysts (PTC) are polar organic complexes, usually quarternary ammonium compounds. The transfer of inorganic anions $(INH)^-$ as inhibitors into an organic phase is easily accomplished by an exchange reaction with the quarternary ammonium salt(1) in the form of an organic complex. This is shown in Figure 1.

The organic complex of this inhibitor molecule could be then conveniently dissolved in any suitable nonpolar organic solvent (carrier vehicle). Since phase transfer of an inorganic compound to an organic complex is through exchange of only anions, the crack arrestment compounds (inhibitors) used must be of anionic nature.

In the present study, the phase transfer catalyst used was Adogen 464 which is a methyl trialkyl (C_8-C_{10}) ammonium chloride. A direct phase transfer method was used to dissolve inorganic compounds in the organic solvents. A 0.1M stock

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(1) Available from Aldrich Chemical Co.

solution of Adogen 464 was prepared in either mineral spirits or xylene and 10 mL of this solution was mixed with approximately 1 gram of solid (inorganic compound). The mixture was thoroughly agitated for 30 minutes and then allowed to settle. The supernatant liquid was decanted and used in the fatigue testing. The solubility of most compounds used in either mineral spirits or xylene was less than 0.2%. Sodium nitrite was approximately 3 to 4 times more soluble. Comparatively, the inhibitors were more soluble in mineral spirits than in xylene.

The compounds tested for crack arrestment were sodium dichromate, sodium nitrite, sodium borate, sodium molybdate, dodecyl alcohol, and AMLGUARD (MIL-C-85054), a hard film forming, water displacing, corrosion preventive compound.

The effect of these compounds was investigated on low cycle corrosion fatigue life of a high strength steel in a high humidity environment. The specimens used were notched bend bars (fracture mechanics type (Figure 2)) fabricated from vacuum arc remelted Type 4340 steel of 260 to 280 ksi ultimate tensile strength. The specimens were fatigue precracked before loading on an Instron machine and enclosed in a humidity controlled plexiglas chamber. Maintenance of high humidity (>90% relative humidity) was simply achieved by bubbling compressed air through several water saturating towers before allowing it to pass into the chamber. For creating a dry test environment (>15% relative humidity), the compressed air was allowed to flow through two drying tubes containing Drierite as a desiccant before it was circulated through the chamber. Usually an hour of preconditioning was sufficient to create a desired level of humidity in the environmental chamber. A three point load configuration was used for cycling the specimen between 150 and 1500 pounds at a frequency to 10 cycles/minute. These conditions yield a minimum fracture mechanics stress intensity factor of approximately 25 ksi $\sqrt{\text{inch}}$ for dry air environment. Except for control tests, all crack arrestment experiments were performed in moist air of >90% relative humidity.

Various candidate compounds, dissolved in an organic solvent as described earlier, were introduced in the notch area of the precracked specimen as a small drop before loading in the Instron. A small drop of crack arrestment compound was also introduced in the inverted notch area after the specimen was loaded. The surface tension of the carrier vehicle (solvent) was sufficient to keep the drop in place in the notch during the test. Capillary action produced by the opening and closing of the crack during the load cycling provided replenishment of the crack arrestment compounds to the tip of the advancing crack. This effect could be easily observed during crack length measurement through a microscope. The crack growth monitoring was done periodically after every 500 cycles to determine the crack growth rate.

The calculation of stress intensity factor at the tip of the crack was made by using the following equation from ASTM E399:

$$K_I = (P_Q . S/B . W^{3/2}) \left[2.9 (a/w)^{1/2} - 4.6 (a/w)^{3/2} + 21.8 (a/w)^{5/2} - 37.6 (a/w)^{7/2} + 38.7 (a/w)^{9/2} \right]$$

where P_Q = maximum load (pounds), S = span length (inches), B = thickness of specimen, W = depth of specimen, and a = crack length + notch depth.

RESULTS AND DISCUSSION

Results of the fatigue crack growth tests on Type 4340 high strength steel in both humid and dry air are summarized in Table I. With no inhibitor present in the notch area of the test specimen (Figure 2), the fatigue life in moist air was found to be less than 2000 cycles as compared to 20,000 cycles in dry air at room temperature. This shows a large effect of environment on the fatigue strength of steel. Results with various candidate crack arrestment compounds are shown in Table I between those of dry and moist air. As apparent from Table I, the formulation containing chromate, nitrite and borate worked best. The results for sodium nitrite and sodium borate showed an improvement in the results, but the effect was less significant. This is simply because chromates are more potent oxidizers than borates and nitrites together. The results obtained from use of palladium and lanthanum also showed a definite gain in the fatigue life of Type 4340 steel. Palladium and rare earths are reported to act as hydrogen getters during cathodic reactions at the tip of the advancing crack,[4] therefore minimizing hydrogen embrittlement effects.

The curves of crack growth rate measured in crack extension/cycle, (da/dn) vs the stress intensity factor (K_I) determined for various environmental conditions and in presence of various candidate compounds are plotted as shown in Figures 3 and 4. A comparative evaluation of the various candidate compounds showed a marked decrease in crack growth rate of Type 4340 steel with all of them. Among them, the combination of chromate + nitrite + borate showed the best results with the crack growth rate reduced to 28 micro inch/cycle as compared to 110 micro inch/cycle in moist air alone. Thus, the crack growth rate was retarded by about a factor of 4. Other compounds, although beneficial, were less effective. AMLGUARD, which worked well in statically loaded tests, failed to perform in the fatigue tests most probably because it primarily forms a hard film that will not seep to the crack tip. The effect of dodecyl alcohol[7,8] was either negative or zero on crack growth rates of the steel in the moist environment.

Dichromate is known to be an excellent anodic oxidizing inhibitor of transition metals through formation of passive films. Borate acts as a corrosion inhibitor by modifying the pH of the corrosive media (raises pH in crevices and cracks to neutral levels). Nitrites act as oxygen scavengers and also help facilitate the passivation process, thus minimizing corrosion. It was for these reasons that a combination of the three worked so well in retarding the crack growth rate. Adding hydride formers or hydrogen getters along with some catalysts which may accelerate the hydrogen recombination reaction to form molecular hydrogen should be considered. Lanthanum, cerium, and palladium compounds have already shown some encouraging results (Table I) in this respect. Since chromates are increasingly being restricted in their applications because of toxicity, other oxidizing compounds were studied for their effectiveness as passivator. The results for hexavalent cerate are encouraging in this respect. Cerium (VI) is a good oxidizer also. Although not as efficient as the dichromate, the cerate compound has shown an increase in the fatigue life of 4340 steel by over a factor of 3. A further improvement in the inhibition of crack propagation would be to use an enhanced carrier solution (e.g., solvent/carrier) to assure proper "wetting" of the advancing crack surface. Although mineral spirits as the solvent in transporting inorganic ions have produced excellent results, the shelf life of the crack arresting compounds with this solvent is reduced. This is because the unsaturated hydrocarbons in the mineral spirits are themselves oxidized by the inorganic oxidizing anions dissolved in them. As an alternative to it, xylene has been found to function as a more stable inhibitor carrier solvent.

The fractured surfaces of the specimens after fatigue tests were examined by scanning electron microscopy (SEM). The micrographs of the specimens shown in Figure 5 represent the area of fractured surfaces lying in between the pre-crack and overload fracture zones. They represent the regions of crack where corrosion fatigue presumably occurs and where the crack growth rate becomes independent of stress intensity factor in the da/dn vs ΔK plots. The micrographs of the specimens shown in Figure 5 demonstrate the differences in the crack morphology of the surfaces as the test medium was changed from a very dry to a high humidity and then to one containing a crack arrestment compound. In the dry air, the fractured surface showed the typical characteristics of fatigue failure (Figure 5, Plates 1a and 1b) with some secondary cracks propagating perpendicular to the direction of crack growth. The center of Plate 1b showed fatigue striations very clerely. In the case of high humidity test environment, the fractographs (Plates 2a and 2b, Figure 5) showed the predominant intergranular brittle fracture with several secondary cracks running parallel to the direction of crack growth. However, when a crack arrestment compound was used on the specimen, such as a mixture of dichromate, nitrite, and borate which worked best, the high humidity effects were counteracted as shown in Plates 3a and 3b (Figure 5). The predominant intergranular cracking observed in high humidity condition almost disappeared and was replaced by a mostly ductile type failure with fewer secondary side cracks and with some even running perpendicular to the plane of crack growth. In many ways, the fracture profile of this inhibitor containing system resembled that of dry air fracture. The presence of some intergranular cracking observed in Plate 3 of Figure 5 is evidence, however, of only partial retardation of crack growth rate. The curves in Figure 3 show the same trend, crack growth rate with the crack arrestment compound being greater than in dry air. In any case, the decrease of intergranular fracture in the presence of crack arrestment compounds is sufficient indication of reduced embrittlement effects from corrosion in high humidity.

C O N C L U S I O N

New inhibitive compounds have been developed which can be applied *in situ* to retard crack propagation. In this study, a technique of phase transfer catalysis has been used to dissolve inorganic compounds in an organic solvent so that the inhibiting molecules could be devoid of their hydration shells. Thus, they could react with the metal surface with less impediments and in greater numbers to become more effective as crack arresting compounds. Using this method, it has been demonstrated that a combination compound containing dichromate, borate and nitrite was successful in retarding the crack growth of Type 4340 steel by a factor of ~ 4 in over 90% relative humidity. Indications are that the crack arrestment compounds help reduce the hydrogen embrittlement effects of the environment.

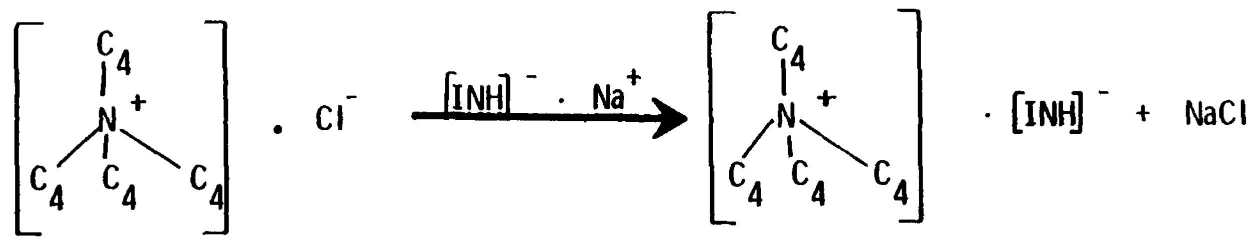
TABLE I

AISI 4340 STEEL CORROSION FATIGUE TEST DATE

ENVIRONMENT (90% R.H.) + CRACK ARRESTMENT COMPOUND	DRY AIR	MOIST AIR	DICHROMATE	NITRITE + BORATE	DICHROMATE + NITRITE + BORATE	MOLYBDATE	AMLGUARD (MIL-C-85054)	DODECYL-ALCOHOL	HEXACHLORO-PALLADATE	LANTHANUM NITRITE	NITRITE + BORATE + CERATE (VI)
CRACK GROWTH RATE AT 35 Ksi $\sqrt{in.}$ (Plateau), IN MICRO IN. PER CYCLE	12	110	42	65	27	61	100	110	45	50	38
STRESS INTENSITY FACTOR AT da/dN OF 100 micro in. per cycle, IN KSI $\sqrt{IN.}$	70	33	52	35	55	50	32	31	$>$ 40	$>$ 40	$>$ 40
CYCLES TO FAILURE, IN KILO CYCLES	17	1.8	6.8	3.3	9.0	4.5	2.3	2	$>$ 4	4.6	$>$ 6

MECHANISM OF PHASE TRANSFER CATALYSIS

Phase Transfer Catalyst (PTC) — Salts of Quaternary Ammonium Complex



Phase Transfer Catalyst (Organic)

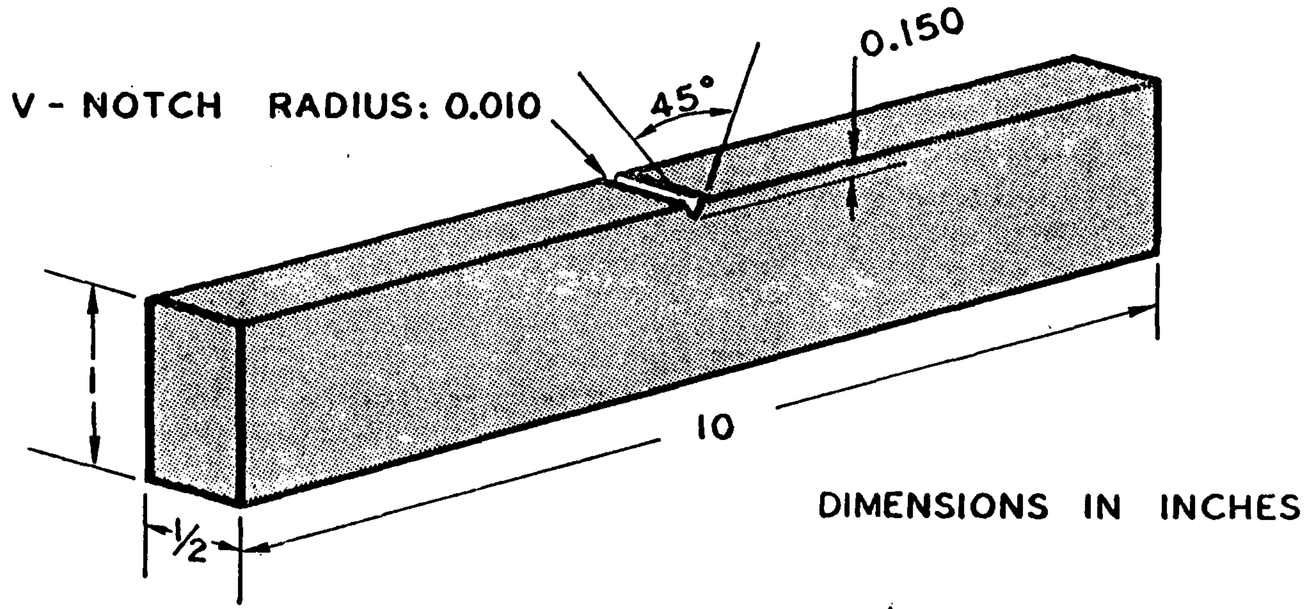
Corossion Inhibitor (Inorganic)

Complex With Inhibitor Anion

Quaternary Ammonium Compounds: Alkyl and Alkyl-Aryl Quaternary Ammonium Hydroxide, Chloride, Bromide and Iodide Salts

PTC Used: Aldrich Chemical Adogen 464-Methyltrialkyl (C_8 - C_{10}) Ammonium Chloride

Figure 1. EXCHANGE REACTION WITH THE QUATERNARY AMMONIUM SALT IN THE FORM OF AN ORGANIC COMPLEX.



B - WITHOUT SIDE GROOVES

Figure 2. NOTCHED BEND BAR SPECIMEN OF TYPE 4340 STEEL WITHOUT SIDE GROOVE.

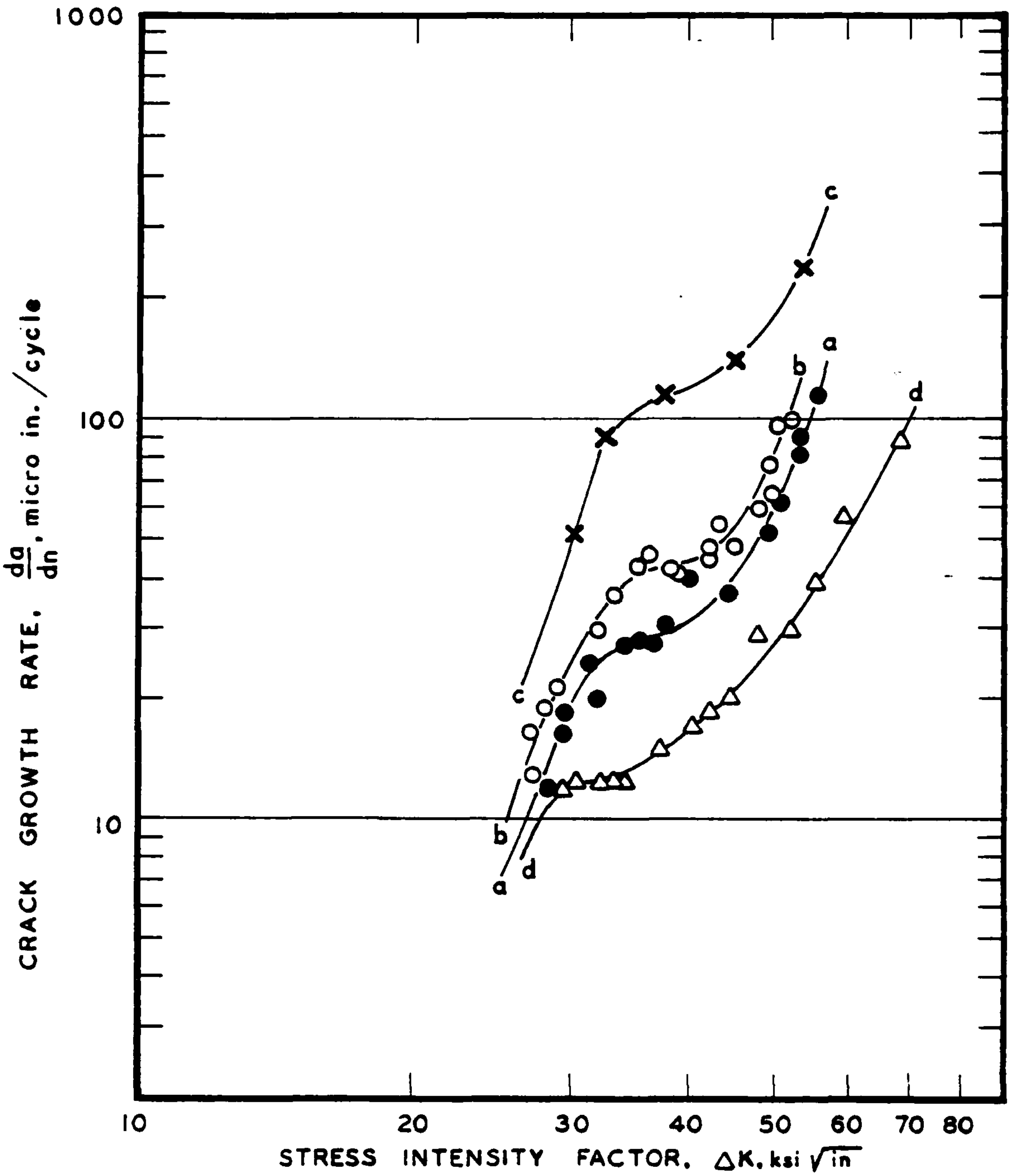


Figure 3. Plots of Crack growth rate (da/dn) vs stress intensity factor (ΔK) for Type 4340 steel in a (a-a) 90% relative humidity + $Na_2Cr_2O_7$ + $NaNO_2$ + $Na_2B_4O_7$; (b-b) 90% relative humidity + $Na_2Cr_2O_7$; (c-c) 90% relative humidity only; (d-d) dry air of <15% relative humidity.

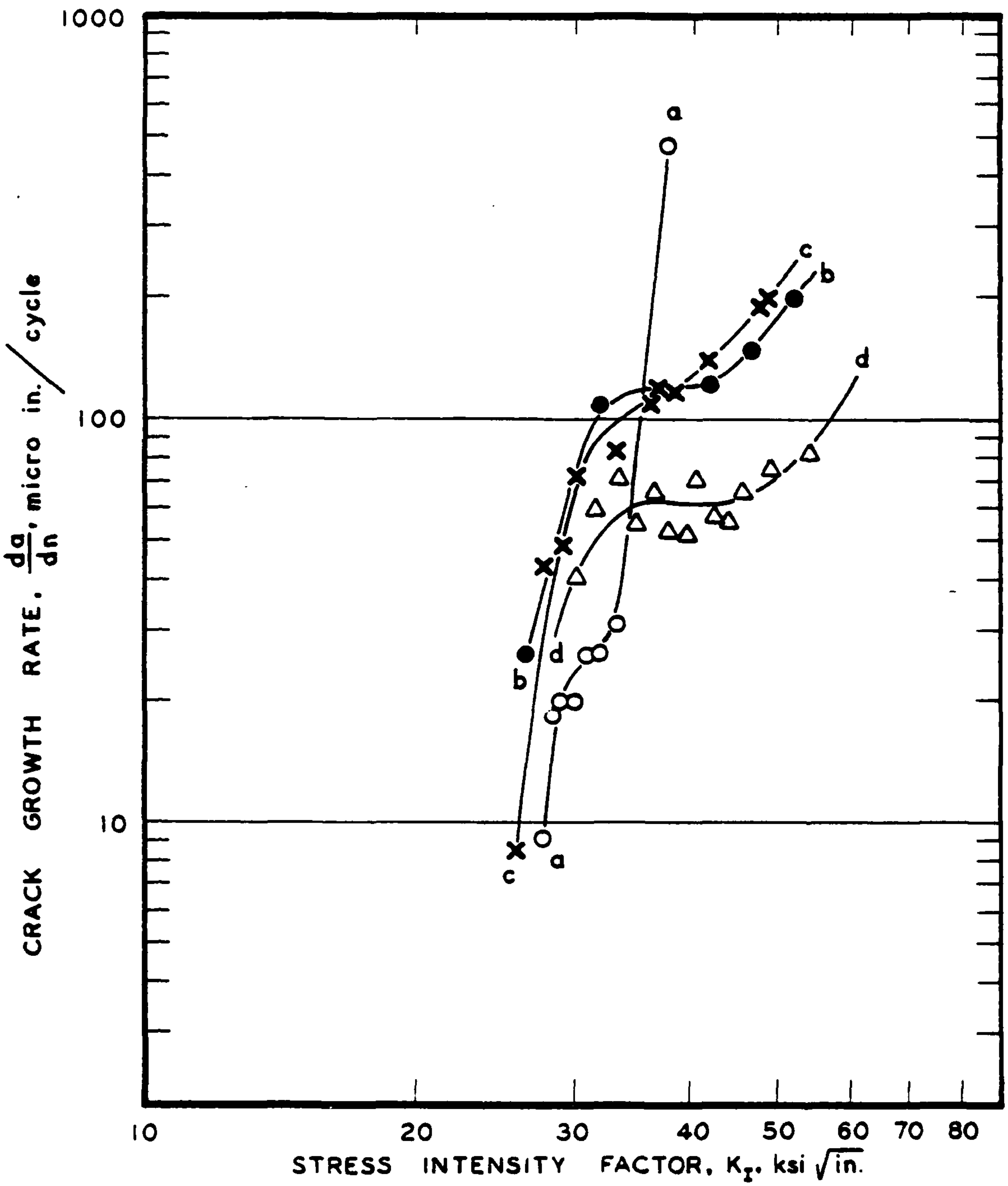


Figure 4. Plots of crack growth rate (da/dN) vs stress intensity factor (ΔK) for type 4340 steel in 90% R.H. and containing (a-a) $Na_2B_4O_7$ + $NaNO_2$; (b-b) Dodecyl alcohol; (c-c) AMLGUARD: and (d-d) Na_2MoO_4 as crack arrestment compounds.

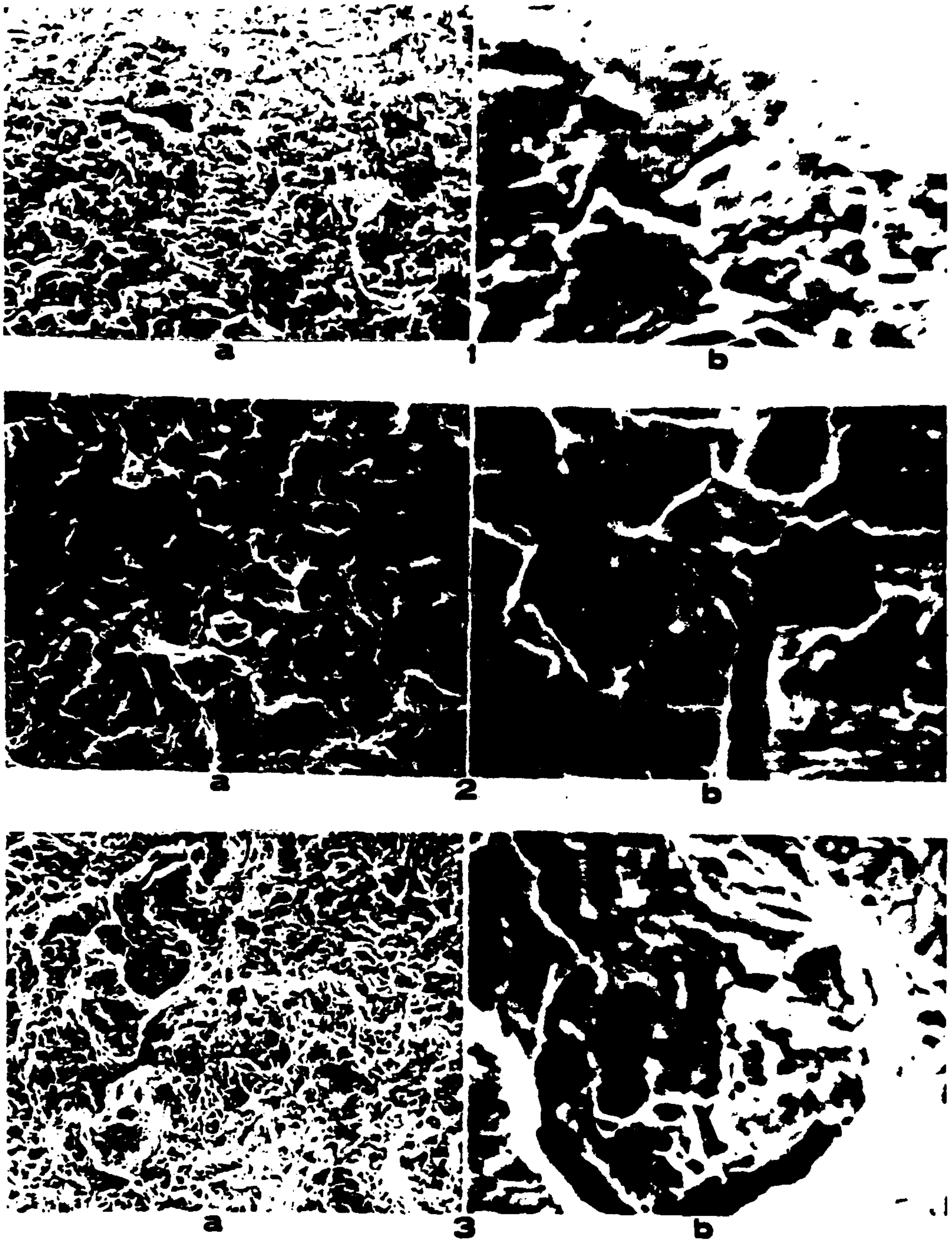


Figure 5. SEM micrographs of fractured surfaces after fatigue tests of Type 4340 steel in: (1) dry air, (2) high humidity, (3) high humidity + crack arrestment compound containing $Na_2Cr_2O_7$ + $Na_2B_4O_7$ + $NaNO_2$. Plates (a) and (b) are at 1000X and 5000X magnification, respectively.

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